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⑤④ **OXYGEN CONCENTRATION PROBE.**

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EP-A- 0 190 829
JP-A- 6 063 464
JP-A- 6 230 959
RUSSIAN CHEMICAL REVIEWS, vol. 41, no. 11,
November 1972, pp. 991-1008, London, GB;
A.T. PHILIPENKO et al.: "Analytical chemistry
of metal complexes with nitrogen-containing
ligands of the 2,2'-bipyridyl type"

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Description

The present invention relates to a probe for measuring the oxygen concentration in a solution or a gas by utilizing quenching by oxygen of luminescence following excitation by light.

5 Heretofore, as for a method for measuring the oxygen concentration in an aqueous solution, there has generally and widely been used an electrochemical method in which an oxygen electrode represented by Clark type one is used and the reduction current of oxygen is measured under a controlled electric potential. However, in this method, since an electric current which flows between two electrodes is measured, the current density cannot be so diminished, and therefore miniaturization of the electrodes to be used is limited. Further, an electric current is generated even in a small extent, and thus it is not proper from the safety aspect to use the method, for example in vivo or in a blood vessel.

In view of these problems, various methods utilizing light for measuring oxygen concentration have been proposed. Since it was reported that pyrenebutyric acid is effective as a fluorescent probe for measuring oxygen concentration (W.M. Vaughan and G. Weber, *Biochem.* 9, 464 (1970)), many researches have been conducted on probes utilizing quenching by oxygen of fluorescence from derivatives of pyrene. Further, another device utilizing pyrenebutyric acid was made (N. Opitz and D.W. Lubbers, *Z. Biomed. Techn.* 28 (31), (1983)). However, in this method it is necessary to use an ultraviolet ray as the exciting ray, so that materials which transmit an ultraviolet ray must be used in the optical system such as a conductor of the exciting ray. When a probe comprising perylene dibutyrate adsorbed on silica gel is used, a visible ray (wave length of 468 nm) can be used as the exciting ray (J.I. Peterson, R.V. Fitzgerald and D.K. Buckhold, *Anal. Chem.* 56, 62 (1984)). However, since this probe greatly suffers from water, it is necessary to protect it with a hydrophobic and oxygen-permeable membrane, which makes the miniaturization thereof more difficult.

Jap. Patent Abstract 9, 199(P-380) (1985), 1922 and JP-A-60-63464 discloses a material for the detection of oxygen in a packaging body. The material comprises a 2- or 4-polyvinylpyridine metal complex which is optionally deposited on a carrier.

With this probe the change in the absorption spectrum of the probe caused by the formation of a complex between the probe and an oxygen molecule is determined, whereby the oxygen concentration is measured.

EP-A-0 204 616 (priority date 30.05.85, publication date 10.12.86) discloses a composition for the detection of oxygen which comprises a colored indicator dissolved in an acceptable solvent. The color of the indicator is changed by the presence of oxygen.

Thus, there is no pre-published description of a probe for measuring oxygen concentration where the exciting ray and luminescence are visible rays and which can stably be used even when it is directly immersed in a liquid to be examined without a protective membrane such as an oxygen-permeable membrane thereon.

EP-A-0 190 829 (priority date 07.02.85, publication date 13.08.86), which is a document according to Art. 54 (3) EPC and relevant for the Contracting States Belgium, Germany, France and United Kingdom, describes a device for monitoring oxygen in an environment in response to light transmitted from a light source comprising: an optical waveguide to receive light transmitted from the light source; and an oxygen-sensitive medium disposed on said waveguide wherein said sensitive medium fluoresces in response to light from said light source, the intensity of fluorescence of said sensitive medium being dependent on the partial pressure of oxygen present in the environment being monitored, said sensitive medium including an oxygen-sensitive fluorescent dye in a plasticized polymer matrix.

Accordingly, an object of the present invention is to provide a probe for measuring oxygen concentrations, which can be used in a method for measuring oxygen concentrations using light but not using an electrochemical method, where the exciting ray and luminescence are visible rays, so that a flexible plastic optical fiber and the like can be used for the conduction of light and also inexpensive materials for visible rays can be used in the optical system, and which can stably be used even when it is directly immersed in a solution and the like without a protective membrane such as an oxygen-permeable membrane, which makes the miniaturization thereof easier.

It has been found that the above object of the present invention is attained by a probe for measuring oxygen concentration according to claim 1.

Fig. 1 is a drawing illustrating an instrument for measuring the luminescence intensity of a probe for the measurement of oxygen concentration. In Fig. 1, 1 represents a quartz plate, 2 represents a fixed membrane of a polypyridine metal complex, 3 represents a quartz cell, and 4 represents a holder made of rubber.

Figs. 2 and 3 are drawings illustrating the relation between the oxygen concentration and the luminescence intensity in a solution to be examined using a probe for measurement of oxygen concentration of the present invention.

Fig. 4 is a drawing illustrating the relation between the oxygen concentration and the luminescence intensity in a gas to be examined using a probe for measurement of oxygen concentration of the present invention.

In the above-described, the probe means any form of instrument for measuring oxygen concentrations comprising an immobilized polypyridine metal complex, including a probe made by molding an immobilized polypyridine metal complex into a desired shape, a probe made by forming a thin film of an immobilized polypyridine metal complex on the surface of a desirably shaped support such as a later-described styrene, silicone or flexible plastic optical fiber, and a probe made by adsorbing a polypyridine metal complex on a desirably shaped support to immobilize the same. Thus, by immobilizing a polypyridine metal complex and measuring the intensity of luminescence thereof, it is possible to know the oxygen concentration in a solution, above all an aqueous solution, or in a gas. A polypyridine metal complex is soluble in water or readily dispersible in water, and cannot stably be used as such in water as a probe for measuring oxygen concentrations.

The present inventors have found that the intensity of the visible luminescence generated by irradiating an immobilized polypyridine metal complex with a visible ray depends on the oxygen concentration in a solution or a gas which is in contact with the complex, and that the relation between the luminescence intensity and the oxygen concentration is represented by the following equation:

$$I_0/I = 1 + K(O_2) \quad (1)$$

wherein I_0 and I are respectively luminescence intensities, provided that I_0 is the luminescence intensity when the oxygen concentration is substantially 0, K is a constant, and (O_2) is the oxygen concentration. Since I_0 and K are constants independent of the oxygen concentration in materials to be examined, it is possible to know the oxygen concentration by measuring the luminescence intensity I .

Various methods are applicable for immobilization of the polypyridine metal complex. Conditions for the immobilization include, (1) that the immobilized metal complex does not dissolve in the liquid to be examined (If dissolved, the luminescence intensity changes, which makes the measurement thereof difficult), (2) that the immobilized metal complex does not suffer an irreversible change by a chemical reaction with the liquid or gas to be examined, and so on.

First, the polypyridine metal complex may most simply be immobilized by dissolving or dispersing the same in a macromolecule.

Many kinds of macromolecules can be used for this purpose. Especially preferred macromolecules include many general purpose plastic usually used such as low density polyethylenes, polypropylenes, polyvinyl chlorides, ethylenevinyl acetate copolymers, polystyrenes, polymethyl methacrylates, silicone resins and polyurethanes. A specific method for introducing the polypyridine metal complex into such macromolecules is conveniently selected according to the kind of macromolecule to be used. For example, there can be used mixing by fusion with heating in case of thermoplastics having a high solvent resistance such as a low density polyethylene, and mixing in a solution (mixing in a solution of a macromolecule in an organic solvent) in case of polystyrene and the like. Proper concentration of the polypyridine metal complex in the mixture with the macromolecule is 1×10^{-8} to 1 mol/dm^3 . In the concentration less than 10^{-8} mol/dm^3 adequate luminescence cannot be obtained and thus the sensitivity is inadequate. On the other hand, in the high concentration exceeding 1 mol/dm^3 , the luminescence intensity does not change in accordance with the oxygen concentration and the probe is not fit for use.

The second method is one in which the polypyridine metal complex is made to be chemically or physically adsorbed on an adsorbent. The adsorbent includes inorganic materials such as silica gels and glasses, organic materials such as porous polymers, various ion exchange resins, and natural materials e.g. polysaccharides and proteins. A cation exchange resin or a chelate type adsorbent can be used to make fixation more stable.

The third method is one in which the polypyridine metal complex is introduced in a macromolecule as a constitutive unit thereof to make a physically and chemically more stable immobilized complex. Although this process requires somewhat complicated procedures compared with the above two methods, it is possible to obtain an immobilized material having the highest stability. Specifically, there may be adopted a method where a polypyridine having a polymerizable functional group is polymerized or copolymerized with a monomer capable of copolymerizing therewith to obtain a polymer or copolymer, and then a metal complex is formed, for example a method where a vinyl compound such as styrene, methacrylic acid, acrylic acid or acrylonitrile is copolymerized with a polypyridine (a ligand) having a vinyl group such as 4-methyl-4'-vinyl-2,2'-bipyridine, and then a metal complex is formed; a method where a monomer having a functional group which is capable of chemically bonding with a substituent of the polypyridine metal complex is polymerized in advance, and then the substituent is bonded to the functional group; and the like. In this connection, the copolymer includes random copolymers, block copolymers, graft copolymers, polymers bridged with the complex and the like.

Proper molar ratio of the monomer to the complex is 1000 to 1, although it is also possible to use the complex only.

It is possible to combine two or more of the above methods. For example, it is also possible to mix the macromolecular complex with another macromolecule.

The polypyridine metal complex is immobilized on a conductor of a visible ray such as a flexible plastic

optical fiber.

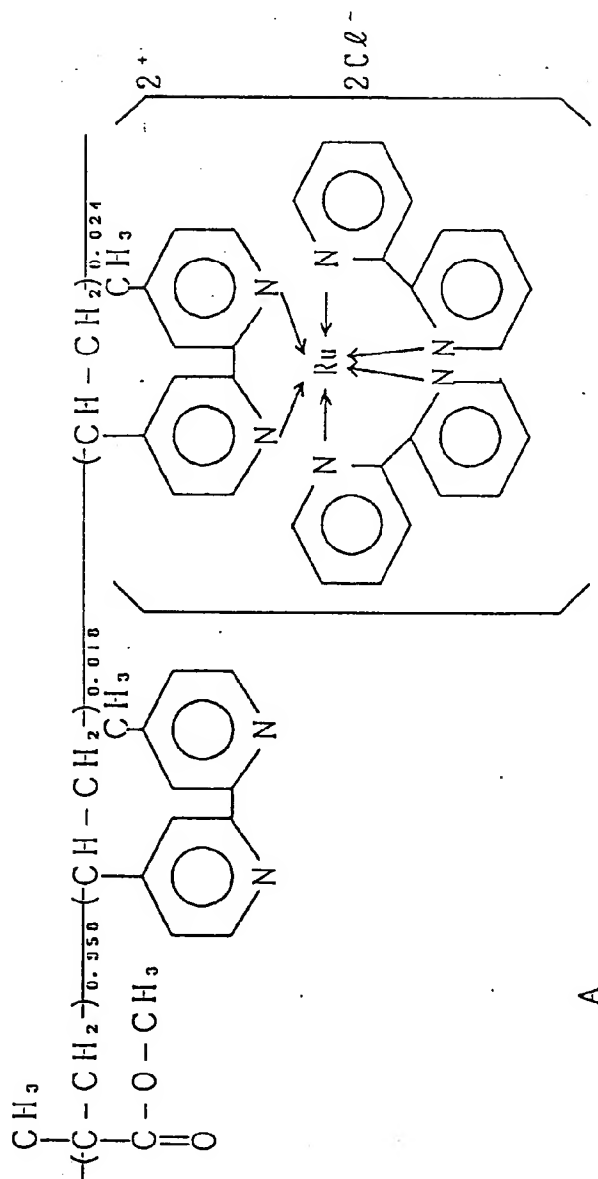
Thus, in order to obtain the immobilized polypyridine metal complex which is chemically or physically more stable, the polypyridine, which is a ligand, is selected from bipyridine, phenanthroline, terpyridine and derivatives thereof. The derivatives are intended to mean a derivative where one or more of hydrogens in the pyridine ring of these polypyridine are independently substituted with other groups, for example alkyl groups, vinyl groups, acetyl groups, halogens, hydroxyl groups or phenyl groups.

Further the metal in the polypyridine metal complex is selected from the group consisting of ruthenium, osmium, chromium, iridium, iron, cobalt, europium and ruthenium is the most desirable. The highest sensitivity is obtained when ruthenium is incorporated. For example, tris(2,2'-bipyridine)ruthenium (II) complex has the absorption maximum of 452 nm, the luminescence maximum of 605 nm and the strong luminescence intensity, and thus is preferably used in the present invention. When this compound is incorporated into a macromolecule, these properties of this complex are hardly changed, and thus the complex may effectively be used.

The following are examples of the present invention.

Example 1

γ -Picoline (Manufactured and sold by Kanto Kagaku Co., Ltd., EP grade reagent) was purified by distillation, and used to prepare 4-methyl-4'-vinyl-2,2'-bipyridine (hereinafter referred to as "Vbpy") according to the known method (P.K. Ghosh and T.G. Spiro, J. Am. Chem. Soc., 102, 5543 (1980)). The Vbpy was purified by a column chromatography (silica gel 40 to 100 mesh, solvent: chloroform/methanol (5/1), both solvents are guaranteed reagents manufactured and sold by Wako Pure Chemical Industries, Ltd.). 0.49 g (2.5 mmol) of this Vbpy and 5 g (50 mmol) of methyl methacrylate (hereinafter referred to as "MMA") which had been subjected to high vacuum distillation in advance were copolymerized in 50 ml of 1,4-dioxane (guaranteed reagent manufactured and sold by Wako Pure Chemical Industries, Ltd.) in the presence of 0.08 g (0.5 mmol) of α , α' -azobisisobutyronitrile (GR grade reagent manufactured and sold by Kanto Chemical Co., Ltd., hereinafter referred to as "AIBN") (in a polymerization tube deaerated and plugged at 60°C for 5 days). One g of the obtained copolymer and 0.15 g of cis-dichlorobis(bipyridine)ruthenium complex (hereinafter referred to as "cis-Ru(bpy)₂Cl₂·4H₂O") synthesized and purified according to the known method (G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch and D.G. Whitten, J. Am. Chem. Soc., 99, 4947 (1977)) were reacted in 700 ml of 1-butanol (guaranteed reagent manufactured and sold by Kanto Chemical Co., Ltd.) under reflux (for 24 hours). The product was evaporated to dryness, extracted with chloroform (guaranteed reagent) and evaporated to dryness again to obtain the final product A. Elementary analysis showed that the product A is a copolymer having the following structure.



A 10% methanol solution of this macromolecular complex was added dropwise on a rectangular quartz plate 1 (thickness 1 mm, length 40 mm, width 8 mm), followed by deaeration and drying while the plate was held horizontal to obtain a transparent reddish orange membrane 2 of the thickness of about 10 μm . The membrane 2 was washed several times with flowing water and held in a whole surface transparent quartz cell 3 (optical path length 1 cm) equipped with a ground-in stopper with a holder 4 made of rubber as shown in Fig. 1, and the cell was filled with physiological saline (a 0.9% aqueous sodium chloride solution).

Argon gas (purity 99.9%) or oxygen gas (purity 99.5%) or a mixed gas thereof (The concentration ratio was made to be arbitrarily set up by the method in which the flow rate ratio is changed) was introduced into the physiological saline in the cell at the flow rate of 50 cc/min for 15 minutes to cause bubbling, whereby the oxygen concentration in the physiological saline was arbitrarily set up from zero to saturation. In this connection, the relation between the mixing ratio of argon/oxygen and the oxygen concentration in the aqueous solution was determined in advance by an oxygen electrode (M-HOS® PO_2 sensor manufactured and sold by Mitsubishi Rayon Co., Ltd.). It was found that a linear relation exists between the oxygen/argon mixing ratio and the oxygen concentration, and the oxygen concentration at the saturation is $1.26 \times 10^{-3} \text{ mol/dm}^3$. The cell was tightly plugged immediately after the gas bubbling, and the luminescence intensity was measured by a luminescence spectrophotometer (MPF-4 type, manufactured and sold by Hitachi, Ltd.). In the measurement, an exciting ray having the wave length of 460 nm was used and the luminescence was measured at the wave

length of 610 nm. Both gas bubbling and measurement of luminescence were conducted at 22°C. The results are shown in Table 1. Linear relation exists between I_0/I and the oxygen concentration as shown in Fig. 2, and thus it is seen that the membrane 2 can be used as a probe for measuring oxygen concentration.

Table 1 Relation between the oxygen concentration and the luminescence intensity (Example 1)

Oxygen concentration		Luminescence intensity	
Introduced gas (%)	In physiological saline*1	(mm) *2	I_0/I
0	0	127.8	1.000
22.7	0.287	113.9	1.122
40.4	0.512	102.6	1.246
62.0	0.785	94.3	1.355
81.2	1.03	86.9	1.471
99.5	1.26	79.4	1.610

*1 Unit mmol/dm^3

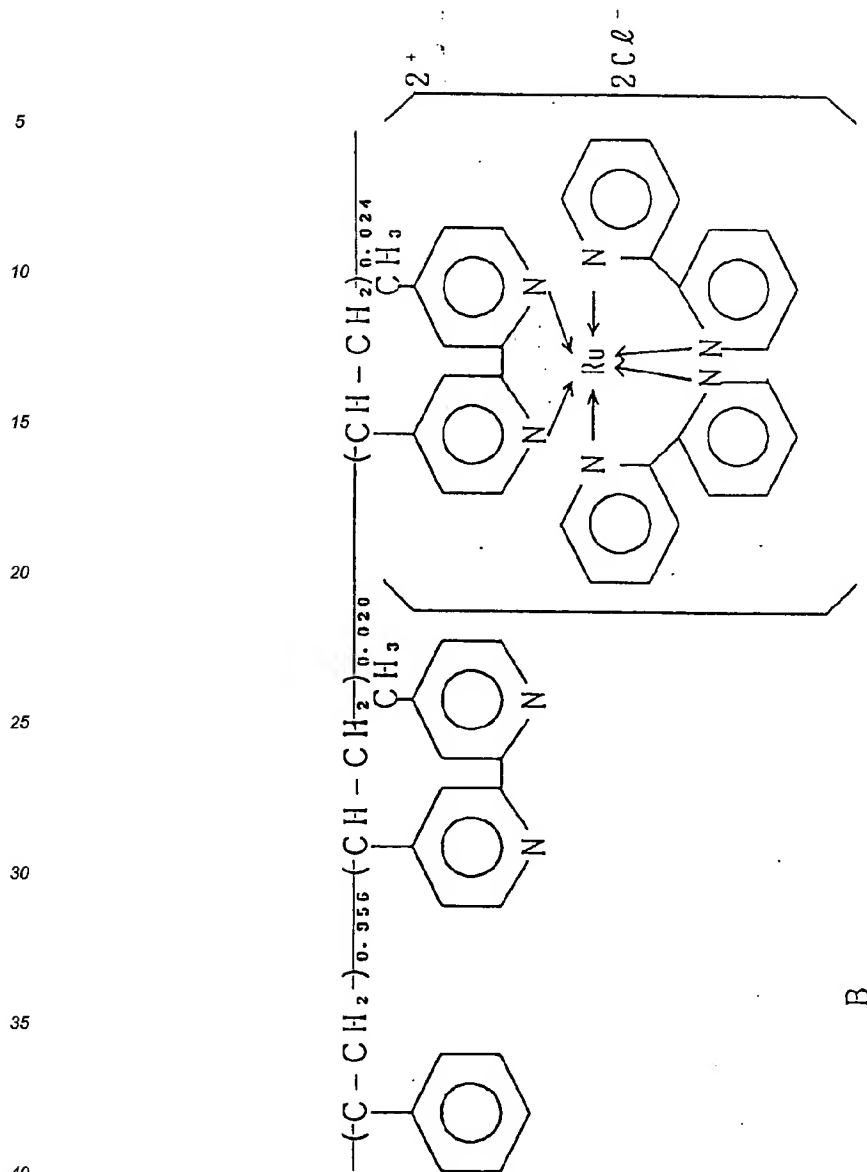
*2 Sensitivity 30 + 5 Scale height at the recorder range of 5 mV

Example 2

Tris(bipyridine)ruthenium complex (hereinafter referred to as " $\text{Ru}(\text{bpy})_3\text{Cl}_2$ ") was obtained from ruthenium chloride anhydride (reagent manufactured by Aldrich Corporation) and bipyridine (reagent manufactured by Aldrich Corporation) according to the known method (C.T. Lin, W. Bottchem, and Chou, J. Am. Chem. Soc., 98, 6536 (1976)). This metal complex was weighed so that the concentration after mixing became 10^{-3} mol/dm^3 , and well mixed with the silicone sealant of a room temperature cross-linking type (SE5001 manufactured by Toray Silicone Co., Ltd.). The mixture was coated on the same quartz plate 1 as that used in Example 1 so that an almost uniform membrane having the thickness of about 0.1 mm was formed. The resulting plate was allowed to stand horizontally in an oven (60°C) for 30 minutes to harden the membrane, whereby a silicone membrane containing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was obtained. After the membrane was several times washed with flowing water, the relation between the oxygen concentration and the luminescence intensity was determined under immersion thereof in physiological saline in the same manner as in Example 1. As a result, a good linear relation between I_0/I and the oxygen concentration was obtained.

Example 3

A copolymer of styrene and Vbpy was obtained in the same manner as in Example 1, and subjected to the same reaction as in Example 1 for forming a complex with ruthenium, whereby the following macromolecular complex B was obtained.



Then, an orange translucent membrane having the thickness of about 10 μm was formed on a quartz plate using the complex B in the same manner as in Example 1. The membrane was set up in the cell 3 for measuring luminescence in the same manner as in Example 1, the cell was filled with methanol (guaranteed reagent, manufactured and sold by Wako Pure Chemical Industries, Ltd.) in place of physiological saline in Example 1. The oxygen concentration in methanol was arbitrarly set and the relation between the oxygen concentration and the luminescence intensity was investigated. As a result, good linear relation was found between I_0/I and the oxygen concentration (Refer to Fig. 3). The concentration at oxygen saturation was supposed to be 9.45 mmol/dm³ ("Kagaku Binran Kisoheii II" (Chemical Handbook Fundamental Volume II) edited by The Chemical Society of Japan, p. II-164).

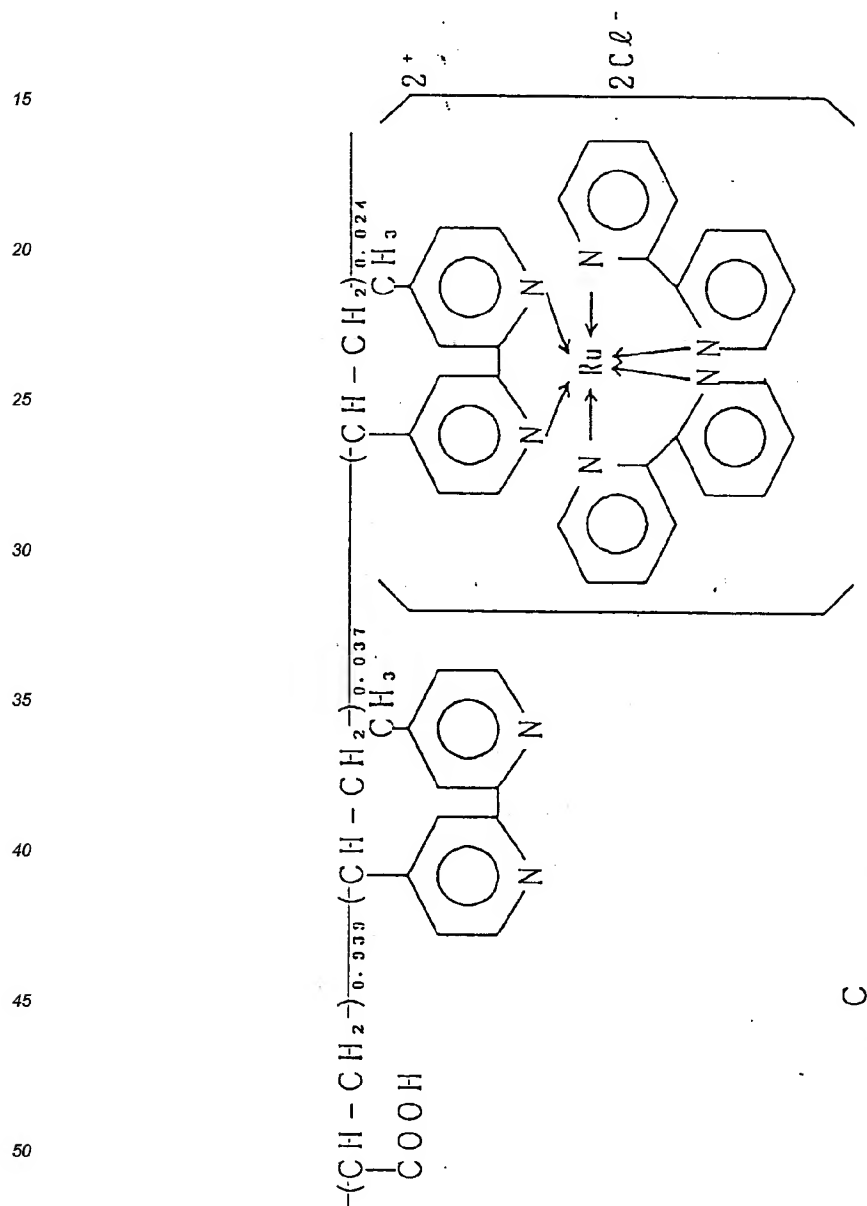
Example 4

A 10 mM aqueous solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ which had been synthesized and purified in Example 2 was prepared. A Nafion 117® membrane (thickness of 0.007 inches, sold by Aldrich Corporation) which is a cation exchanger was immersed in the solution for 10 hours, taken out therefrom, washed several times with water and dried at room temperature for 24 hours to obtain an orange Nafion® membrane which adsorbed $\text{Ru}(\text{bpy})_3^{2+}$. This membrane was stuck on the same quartz plate as in Example 1 with a pressure sensitive adhesive double-

coated tape. The resulting plate was fixed in a cell in the same manner as in Example 1 and the relation between the luminescence intensity and the oxygen concentration in physiological saline was determined. Good linear relation was found between I_0/I and the oxygen concentration.

Example 5

Vbpy and acrylic acid (guaranteed reagent, manufactured and sold by Wako Pure Chemical Industries, Ltd. and distilled under high vacuum) were copolymerized in the same manner as in Example 1, and $\text{cis-Ru(bpy)}_3\text{Cl}_2$ was reacted with the resulting copolymer to obtain a macromolecular complex C of the following formula:



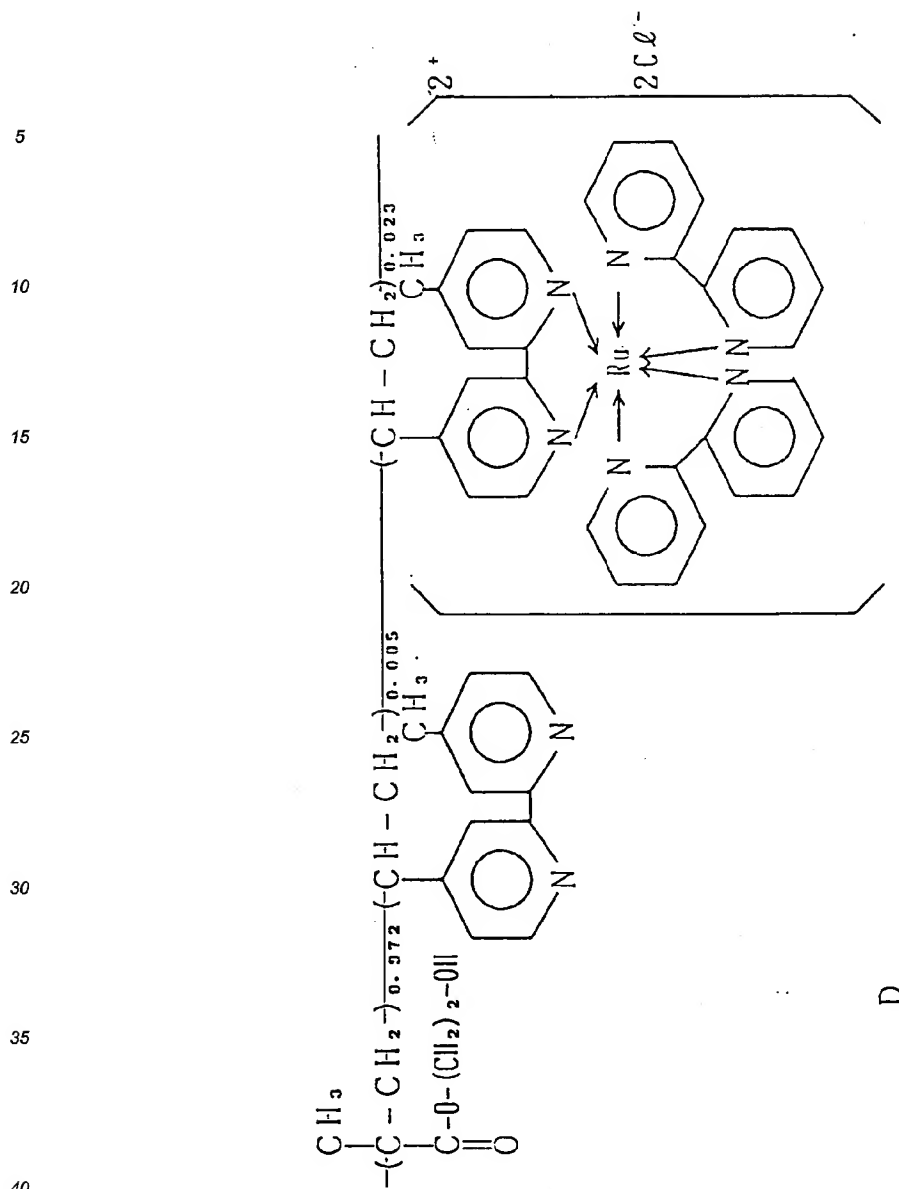
Purification was carried out by dialysis of an aqueous solution thereof (48 hours). A 5% methanol solution of this macromolecular complex was prepared, and Nafion 117® was immersed therein, washed with water, dried and used for measurement of the luminescence intensity in physiological saline in the same manner as in Example 4, except that measurement of the luminescence was conducted at 610 nm. The results revealed a good linear relation between I_0/I and the oxygen concentration.

Example 6

Tris(1,10-phenanthroline)ruthenium complex perchlorate trihydrate (hereinafter referred to as "Ru-(phen)₃(ClO₄)₂·3H₂O" was synthesized and purified according to the known method (C.T. Lin, et al., J. Am. Chem. Soc., 98, 6536 (1976)). A chelate filter paper having an iminodiacetic acid group (manufactured and sold by Sumitomo Chemical Co., Ltd.) was immersed in a 10 mM aqueous solution thereof (10 hours), washed with water and dried to obtain a chelate paper on which Ru(phen)₃²⁺ was adsorbed. This paper was fixed in cell 3 and the luminescence intensity in physiological saline was measured, in the same manner as in Example 4, except that the wave length of the exciting ray was 450 nm and measurement of the luminescence was conducted at the wave length of 600 nm. A good linear relation was found between I₀/I and the oxygen concentration, as was found in the preceding examples.

Example 7

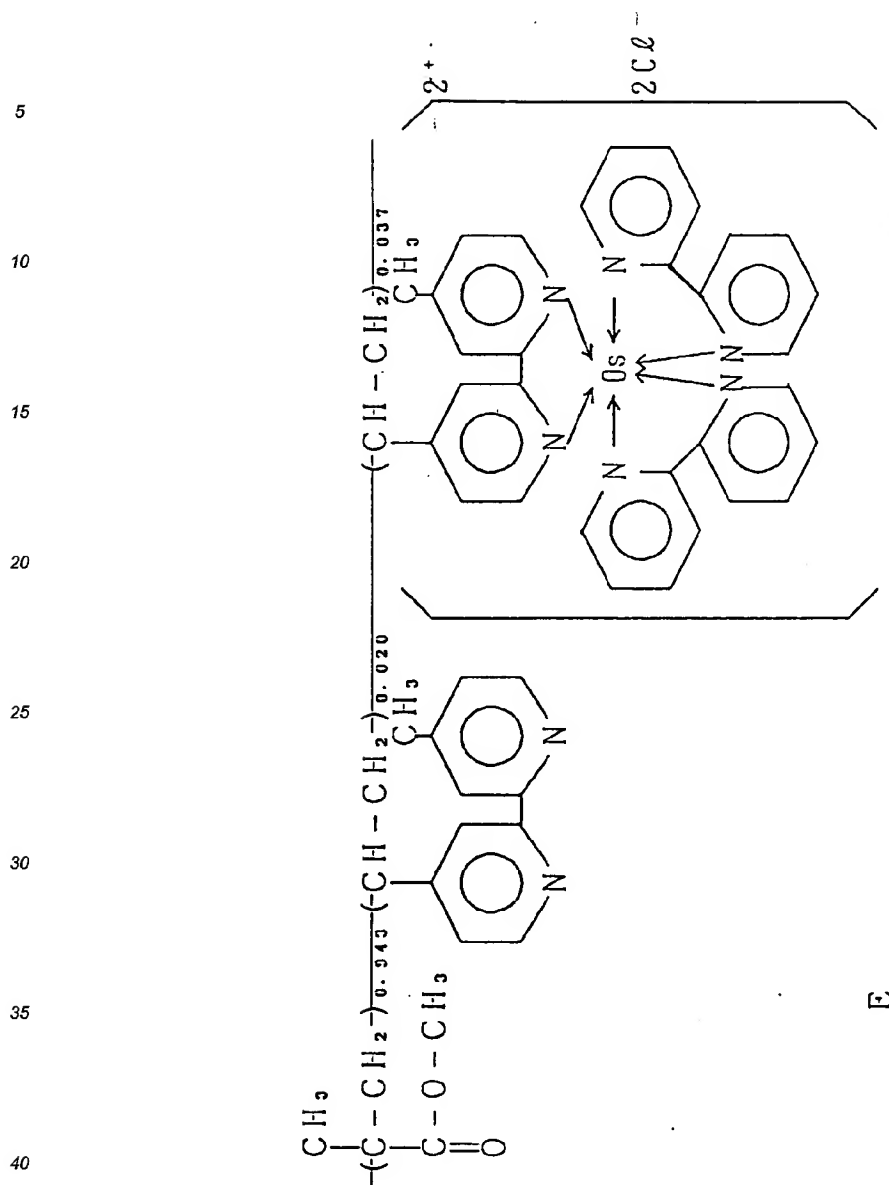
According to the same method as in Example 1, 2-hydroxyethyl methacrylate (EP grade reagent, manufactured and sold by Kanto Chemical Co., Ltd., hereinafter referred to as "HEMA") as subjected to high vacuum distillation in advance and Vbpy were copolymerized, and the resulting copolymer was reacted with cis-Ru(bpy)₂Cl₂ to obtain the macromolecular complex D of the following formula:



45 A 1 mmol/dm³ (based on Ru) aqueous solution of this macromolecular complex was prepared, and gelatin (reagent manufactured by Aldrich Corporation) derived from pig hides was added to this solution to make the concentration of 10%. The mixture was heated to dissolve the gelatin, poured in a laboratory dish (made of glass, 15 mmφ) which was horizontally held, cooled, solidified, and dried in a desiccator. The thus obtained gelatin membrane (thickness of about 0.1 mm) containing the macromolecular complex D was cut into a size 40 mm long and 8 mm wide, and fixed on quartz plate 1 through a pressure sensitive adhesive double-coated tape. The relation between the luminescence intensity and the oxygen concentration in physiological saline was investigated, and the results revealed a good linear relation between I_0/I and the oxygen concentration in the aqueous solution.

Example 8

55 The copolymer of MMA and Vbpy which was synthesized and purified in Example 1, and cis-dichlorobis(bipyridine)osmium complex which was synthesized by the known method (D.M. Klassen et al., J. Chem. Phys., 48, 1853 (1968)) were reacted in the same manner as in Example 1 to obtain the macromolecular complex E of the following formula:



A membrane was formed on quartz plate 1 using this macromolecular complex E in the same manner as in Example 1 to obtain an orange membrane of about 10 μm thick. This membrane was held in a cell for measurement of luminescence. The cell was filled with physiological saline, and the relation between the oxygen concentration and the luminescence intensity was investigated, in the same manner as in Example 1 except that an exciting ray having the wave length of 460 nm was used and measurement of the luminescence was conducted at the wave length of 600 nm. A linear relation was found between I_0/I and the oxygen concentration. However, the luminescence intensity was lower and the deviation from a straight line was somewhat larger than the case in Example 1.

Example 9

A 10 mmol/dm³ aqueous solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ which had been synthesized and purified in Example 2 was prepared, and a filter paper (No.1, manufactured and sold by Toyo Filter Paper Co., Ltd.) was immersed therein, taken out after 30 minutes, washed with water and dried at room temperature for 24 hours to obtain a filter paper on which $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was adsorbed. This filter paper was cut into rectangle pieces of 40 mm long, 8 mm wide, which were fixed on a glass plate (40 mm long, 8 mm wide and 1 mm thick), and held in a

cell for measuring luminescence in the same manner as in Example 1. A mixed gas of oxygen/argon prepared in arbitrary mixing ratios was introduced in the cell at 50 ml/min, the cell was tightly plugged 15 minutes thereafter, and the luminescence intensity in a mixed gas containing oxygen was measured, in the same manner as in Example 1 except that an exciting ray having the wave length of 460 nm and the luminescence was measured at the wave length of 605 nm. A good linear relation was obtained between I_0/I and the oxygen concentration.

As seen from the foregoing, the probe for measuring oxygen concentration of the present invention is one which can be used even in a case where the exciting ray to be used therefor and the luminescence and visible rays, so that it is possible to use a flexible plastic fiber and the like as the conductor of light and also to use inexpensive materials for visible rays in the optical system. Further, the present probe can stably be used even when it is directly immersed in a solution and the like without a protective membrane such as an oxygen-permeable membrane, which makes miniaturization thereof easier.

Claims

Claims for the following Contracting States : BE, DE, FR, GB

1. A probe for measuring the oxygen concentration in a solution or a gas by utilizing quenching by oxygen of luminescence following the excitation of molecules by irradiation with light, wherein said probe comprises an immobilized polypyridine metal complex, the polypyridine metal complex is immobilized on a conductor for a visible ray, the metal of the polypyridine metal complex is selected from ruthenium, osmium, iridium, iron, chromium, cobalt and europium, and a ligand of the polypyridine metal complex is selected from bipyridine, phenanthroline, terpyridine and derivatives thereof, provided that the immobilized polypyridine metal complex is not applied to an optical fiber when it is dissolved or dispersed in a Plasticized polymer matrix.
2. A probe for measuring the oxygen concentration of claim 1, wherein the polypyridine metal complex is immobilized by being dissolved or dispersed in a macromolecule.
3. A probe for measuring the oxygen concentration of claim 1, wherein the polypyridine metal complex is immobilized by being adsorbed on an adsorbent.
4. A probe for measuring the oxygen concentration of claim 1, wherein the polypyridine metal complex is immobilized by being introduced in a macromolecule as a constitutive unit thereof.

Claims for the following Contracting States : CH, IT, LI, NL, SE

1. A probe for measuring the oxygen concentration in a solution or a gas by utilizing quenching by oxygen of luminescence following the excitation of molecules by irradiation with light, wherein said probe comprises an immobilized polypyridine metal complex, the polypyridine metal complex is immobilized on a conductor for a visible ray, the metal of the polypyridine metal complex is selected from ruthenium, osmium, iridium, iron, chromium, cobalt and europium, and a ligand of the polypyridine metal complex is selected from bipyridine, phenanthroline, terpyridine and derivatives thereof.
2. A probe for measuring the oxygen concentration of claim 1, wherein the polypyridine metal complex is immobilized by being dissolved or dispersed in a macromolecule.
3. A probe for measuring the oxygen concentration of claim 1, wherein the polypyridine metal complex is immobilized by being adsorbed on an adsorbent.
4. A probe for measuring the oxygen concentration of claim 1, wherein the polypyridine metal complex is immobilized by being introduced in a macromolecule as a constitutive unit thereof.

Patentansprüche**Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB**

- 5 1. Fühler zur Messung der Sauerstoffkonzentration in einer Lösung oder einem Gas unter Ausnutzung der Lumineszenzauslöschung durch Sauerstoff, nach der Anregung von Molekülen durch Bestrahlen mit Licht, umfassend einen immobilisierten Polypyridinmetallkomplex, wobei der Polypyridinmetallkomplex auf einem Leiter für sichtbare Strahlen immobilisiert ist, das Metall des Polypyridinmetallkomplexes gewählt wird aus Ruthenium, Osmium, Iridium, Eisen, Chrom, Kobalt und Europium, und ein Ligand des Polypyridinmetallkomplexes, aus Bipyridin, Phenanthrohn, Terpyridin und Derivaten davon gewählt wird, mit der Maßgabe, daß der immobilisierte Polypyridinmetallkomplex nicht auf eine optische Faser aufgebracht wird, wenn er in einer weichgemachten Polymermatrix gelöst oder dispergiert ist.
- 10 2. Fühler zur Messung der Sauerstoffkonzentration nach Anspruch 1, wobei der Polypyridinmetallkomplex durch Lösen oder Dispergieren in einem Makromolekül immobilisiert wird.
- 15 3. Fühler zur Messung der Sauerstoffkonzentration nach Anspruch 1, wobei der Polypyridinmetallkomplex durch Adsorbieren an einem Adsorbtionsmittel immobilisiert wird.
- 20 4. Fühler zur Messung der Sauerstoffkonzentration nach Anspruch 1, wobei der Polypyridinmetallkomplex durch Einführen in ein Makromolekül als aufbauende Einheit davon immobilisiert wird.

Patentansprüche für folgende Vertragsstaaten : CH, IT, LI, NL, SE

- 25 1. Fühler zur Messung der Sauerstoffkonzentration in einer Lösung oder einem Gas unter Ausnutzung der Lumineszenzauslöschung durch Sauerstoff, nach der Anregung von Molekülen durch Bestrahlen mit Licht, umfassend einen immobilisierten Polypyridinmetallkomplex, wobei der Polypyridinmetallkomplex auf einem Leiter für sichtbare Strahlen immobilisiert ist, das Metall des Polypyridinmetallkomplexes gewählt wird aus Ruthenium, Osmium, Iridium, Eisen, Chrom, Kobalt und Europium, und ein Ligand des Polypyridinmetallkomplexes, aus Bipyridin, Phenanthrohn, Terpyridin und Derivaten davon gewählt wird.
- 30 2. Fühler zur Messung der Sauerstoffkonzentration nach Anspruch 1, wobei der Polypyridinmetallkomplex durch Lösen oder Dispergieren in einem Makromolekül immobilisiert wird.
- 35 3. Fühler zur Messung der Sauerstoffkonzentration nach Anspruch 1, wobei der Polypyridinmetallkomplex durch Adsorbieren an einem Adsorbtionsmittel immobilisiert wird.
- 40 4. Fühler zur Messung der Sauerstoffkonzentration nach Anspruch 1, wobei der Polypyridinmetallkomplex durch Einführen in ein Makromolekül als aufbauende Einheit davon immobilisiert wird.

Revendications**Revendications pour les Etats contractants suivants : BE, DE, FR, GB**

- 45 1. Sonde de mesure de la concentration en oxygène d'une solution ou d'un gaz par utilisation de l'extinction par l'oxygène de la luminescence après l'excitation de molécules par irradiation avec de la lumière, où ladite sonde comprend un complexe métallique de polypyridine immobilisé, le complexe métallique de polypyridine est immobilisé sur un conducteur d'un rayon visible, le métal du complexe métallique de polypyridine est choisi parmi le ruthénium, l'osmium, l'iridium, le fer, le chrome, le cobalt et l'euporium, et un ligand du complexe métallique de polypyridine est choisi parmi la bipyridine, la phénanthroline, la terpyridine et leurs dérivés, sous réserve que le complexe métallique de polypyridine immobilisé ne soit pas appliqué à une fibre optique lorsqu'il est dissous ou dispersé dans une matrice de polymère plastifié.
- 50 2. Sonde de mesure de la concentration en oxygène de la revendication 1, où le complexe métallique de polypyridine est immobilisé par dissolution ou dispersion dans une macromolécule.
- 55 3. Sonde de mesure de la concentration en oxygène de la revendication 1, où le complexe métallique de polypyridine est immobilisé par adsorption sur un adsorbant.

4. Sonde de mesure de la concentration en oxygène de la revendication 1, où le complexe métallique de polypyridine est immobilisé par introduction dans une macromolécule sous forme d'un motif constitutif de celle-ci.

5 **Revendications pour les Etats contractants suivants : CH, IT, LI, NL, SE**

1. Sonde de mesure de la concentration en oxygène d'une solution ou d'un gaz par utilisation de l'extinction par l'oxygène de la luminescence après l'excitation de molécules par irradiation avec de la lumière, où ladite sonde comprend un complexe métallique de polypyridine immobilisé, le complexe métallique de polypyridine est immobilisé sur un conducteur d'un rayon visible, le métal du complexe métallique de polypyridine est choisi parmi le ruthénium, l'osmium, l'iridium, le fer, le chrome, le cobalt et l'euporium, et un ligand du complexe métallique de polypyridine est choisi parmi la bipyridine, la phénanthroline, la terpyridine et leurs dérivés.
2. Sonde de mesure de la concentration en oxygène de la revendication 1, où le complexe métallique de polypyridine est immobilisé par dissolution ou dispersion dans une macromolécule.
3. Sonde de mesure de la concentration en oxygène de la revendication 1, où le complexe métallique de polypyridine est immobilisé par adsorption sur un adsorbant.
4. Sonde de mesure de la concentration en oxygène de la revendication 1, où le complexe métallique de polypyridine est immobilisé par introduction dans une macromolécule sous forme d'un motif constitutif de celle-ci.

Fig. 1

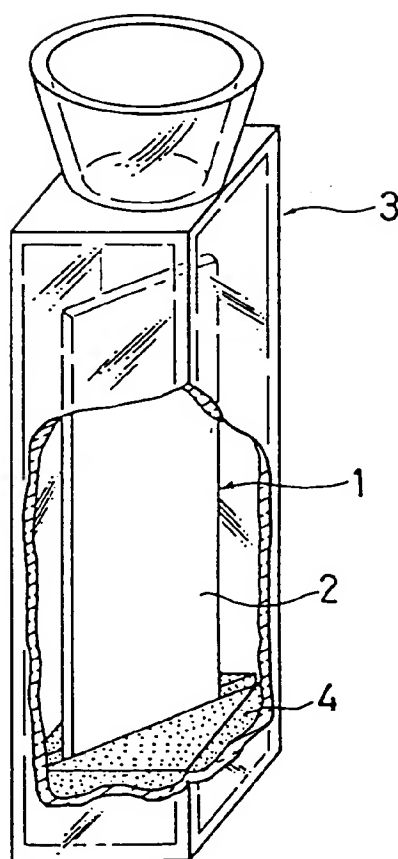


Fig. 2

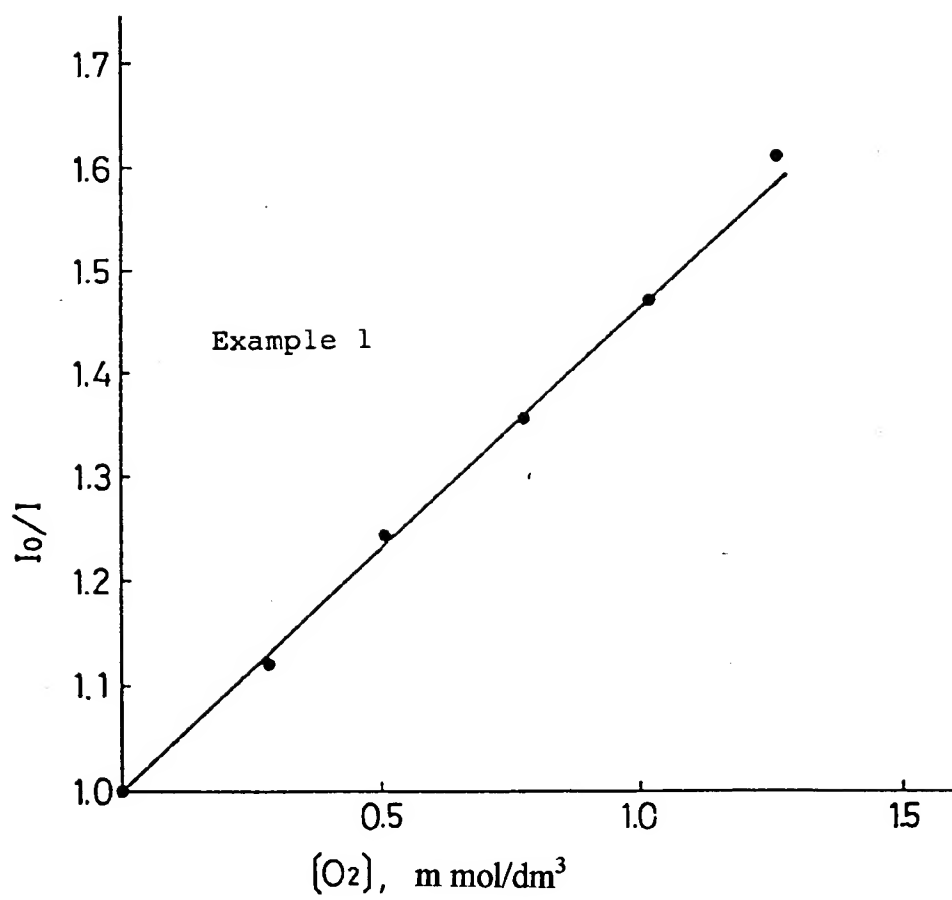


Fig. 3

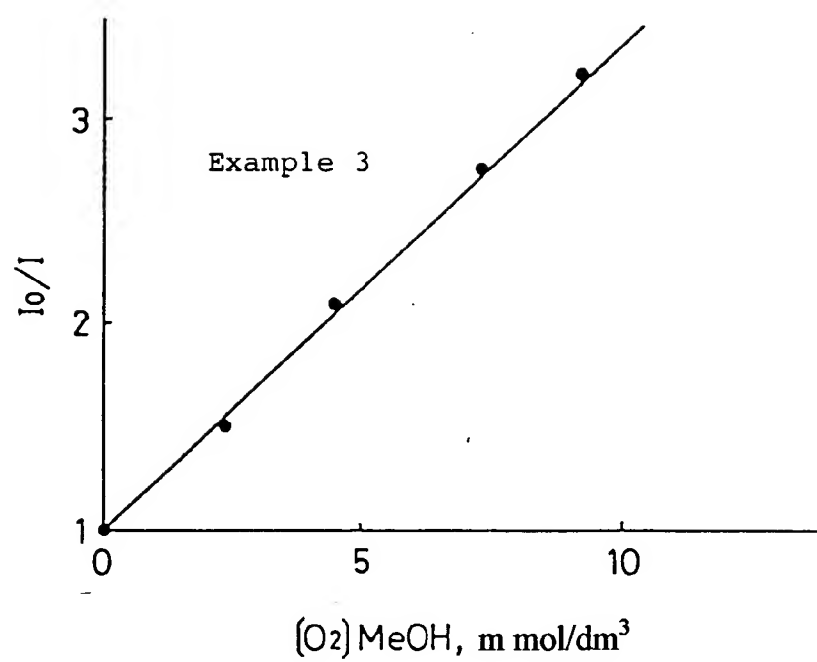


Fig. 4

